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Determination of organochlorine pesticides in seawater using liquid-phase hollow fibre membrane microextraction and gas chromatography–mass spectrometry

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Abstract

The use of hollow fibre membrane microextraction in analytical chemistry has been increasing as the technique is a simple and efficient method for the extraction of trace organic compounds from environmental matrices. A simple liquid-phase microextraction technique using a hollow fibre membrane in conjunction with gas chromatography–mass spectrometry has been developed for the extraction and analysis of organochlorine pesticides (OCPs), i.e. α-hexachlorocyclohexane (BHC), lindane, β-BHC, heptachlor, aldrin, dieldrin, endrin, endosulfan, *p,p′*-DDD, *p,p′*-DDT, endrin aldehyde and methoxychlor, from seawater. The technique requires minimal sample preparation time and solvent consumption, and represents a significant advantage over conventional analytical methods. Optimum extraction conditions have been evaluated with respect to sample pH, salt content and stirring rate, as well as solvent type and extraction time. A high level of detection linearity (coefficient of >0.9995, less than 14% RSD) was obtained for OCPs over a range of analyte concentrations between 5 and 100 μg l^{-1}, with detection limits in the parts per trillion (ppt) to sub-parts per billion range. Comparison between liquid-phase microextraction with hollow fibre membrane and US Environmental Protection Agency Method 508 showed that the novel method has comparable detection limits of between 0.013 and 0.059 μg l^{-1} in seawater.

Keywords: Water analysis; Environmental analysis; Hollow-fiber membranes; Extraction methods; Liquid-phase microextraction; Pesticides; Organochlorine compounds

1. Introduction

Public concern over organochlorine pesticide (OCP) contamination of the environment has risen over recent decades to the extent that it has now become a significant food safety issue. These chemicals are known to disrupt the hormone endocrine system and induce cancer in a range of organisms, thereby posing a significant risk to natural ecosystems and human health [1]. The use of OCPs is tightly regulated in the developed world, but OCPs, including DDT and hexachlorocyclohexane are still widely used in many developing countries for agriculture and disease control [2]. OCPs have a very low solubility in water, are fat soluble, resist metabolic degradation and have a propensity to bioac-

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cumulate in the food chain. High concentrations of OCPs have been detected in bird raptors, marine mammals and human breast milk [3,4].

OCPs can be extracted from aqueous matrices using a variety of conventional techniques including liquid–liquid extraction (LLE) [5] and solid-phase extraction (SPE) [6]. These techniques, whilst offering excellent recovery and analytical precision of OCPs, are also time consuming, expensive and, especially in relation to LLE, hazardous to health due to the high volume of toxic solvents used [7]. Solid-phase microextraction (SPME) [8–10] and liquid-phase microextraction (LPME) using single drop solvent [11–13] are more recent extraction procedures that have been developed for extraction of OCPs from aqueous samples. Although both of these techniques have advantages over conventional methods with respect to solvent consumption, extraction fibres used in SPME are expensive and fragile [14]. Whilst LPME minimizes solvent use and has a high extraction efficiency for aqueous samples, high sample stirring speed can compromise the solvent drop. LPME, compared to SPME, gives less reproducible results [15] and in our previous study [11] we faced difficulties in maintaining a solvent drop in seawater due to sample salinity. LPME using hollow fibre membranes has been developed to overcome these problems. Hollow fibre membrane is widely used for online monitoring of organic compounds, and has been recently studied as a method for direct sample injection into a mass spectrometer [16,17]. Several studies have demonstrated the application of hollow fibres for analytical separations [18], as well as for biotechnological [19] and microbiological [20] applications. LPME using hollow fibre membrane is a simple and inexpensive technique for water analysis, as only a few microlitres of solvent are required [21,22]. As OCPs have high octanol–water partition coefficient (K_{ow}) values (Table 1) that lead to a decrease in solubility in aqueous medium, the analytes can be readily extracted by the solvent-impregnated membrane.

The objective of this study was to develop a simple, efficient extraction procedure for the measurement of OCPs in seawater. The procedure was based on the use of LPME in conjunction with a polypropylene hollow fibre membrane filled with an immiscible solvent and immersed into a stirred aqueous sample. As a result of ''solution diffusion'', analytes diffuse through the membrane and undergo mass transfer into the solvent prior to GC–MS analysis [23,24]. A preliminary analysis on the concentration of selected OCPs in coastal water collected from the Straits of Johor, which lies between Singapore and the southern tip of peninsular Malaysia, was undertaken using the optimised LPME procedure.

2. Experimental

2.1. Standard and reagents

All pesticides used for experimentation were purchased from PolyScience (Niles, IL, USA). HPLC-grade solvents were purchased from Merck

Table 1
GC–MS-SIM conditions for OCPs with octanol–water partition coefficient (log K_{ow}) values

Pesticide	Retention time (min)	Quantitation ion (m/z)	Confirmation ion (m/z)	Log K_{ow}
α-BHC	17.50	181.00	183, 219	3.46
Lindane	18.30	181.00	183, 219	2.8
β-BHC	18.80	227.00	181, 238	3.8
Heptachlor	20.00	272.00	274, 237	4.4
Aldrin	20.70	263.00	293, 265	5.17
Dieldrin	23.17	235.00	246, 318	3.69
Endrin	23.50	317.00	245, 263	3.21
Endosulfan	23.60	207.00	195, 241	3.62
p,p'-DDD	23.81	235.00	237, 165	5.6
p,p'-DDT	24.50	235.00	165, 176	4.89
Endrin aldehyde	25.50	345.00	67, 281	–
Methoxychlor	25.70	227.00	274, 152	3.31

(Darmstadt, Germany). Purified water was obtained from a Milli-Q system (Millipore, Milford, MA, USA). A standard stock solution containing 12 OCPs, i.e. α-hexachlorocyclohexane (BHC), lindane, β-BHC, heptachlor, aldrin, dieldrin, endrin, endosulfan, *p,p′*-DDD, *p,p′*-DDT, endrin aldehyde and methoxychlor, was prepared in acetone at a concentration of 10 mg l^{-1} per pesticide. A working standard solution of 1 μg ml^{-1} per pesticide was prepared by stock dilution in acetone. An artificial seawater sample using natural sea salt (Coral Reef Red sea salt, obtained from Red Sea Fish Pharm (P), Eilat, Israel) dissolved in deionised water to a salinity of 3%, conductivity 49.8 mS and pH 8.25, was prepared for the spiking experiments. Q3/2 Accurel KM polypropylene hollow fibre membrane (Membrana, Wuppertal, Germany) was used for microextraction purposes. The inner diameter of the hollow fibre is 600 μm, the thickness of the wall is 200 μm and the pore size is 0.64 μm.

2.2. Liquid-phase microextraction

A 10-μl microsyringe, with a cone tipped needle (0.47 mm O.D.) (Hamilton, Reno, NV, USA), was used for OCP microextraction. The syringe needle was tightly fitted with a both side open 1.3 cm length of polypropylene hollow fibre membrane. The experimental set-up is illustrated in Fig. 1. The hollow fibre was impregnated with a 5-μl aliquot of toluene

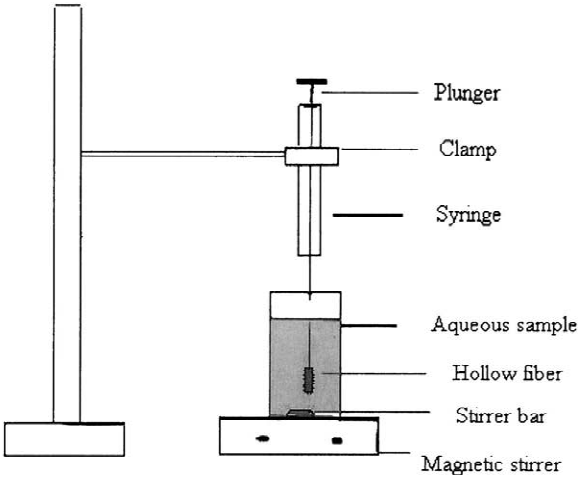

Fig. 1. Schematic of experimental set-up of LPME using hollow fibre membrane.

for 3 s to open membrane pores and then immersed into 5 ml of sample which was subjected to magnetic rotation in a 5-ml volumetric flask. Following OCP extraction, the syringe plunger was depressed so that the hollow fibre was filled with solvent. Extraction took place between the sample and solvent-containing porous fibre for 30 min. Following sample extraction, the magnetic stirrer was switched off and the solvent in the hollow fibre was withdrawn into the syringe. The needle/hollow fibre assembly was then removed from the volumetric flask and the hollow fibre discarded. The syringe plunger was then depressed until 1 μl of the extract remained in the syringe. The extract was then injected into a GC–MS.

2.3. GC–MS analysis

Sample analysis was carried out using a Shimadzu (Tokyo, Japan) QP5050 GC–MS equipped with a Shimadzu AOC-20i autosampler and a DB-5 fused-silica capillary column (30 m×0.32 mm I.D., film thickness 0.25 μm, J&W Scientific, Folsom, CA, USA). Helium was used as the carrier gas at a flow-rate of 1.5 ml min^{-1} and a split ratio of 20. The 1-μl sample was injected into the GC–MS in splitless mode with an injection time of 2 min. The injection temperature was set at 250 °C, and the interface temperature at 280 °C. The GC–MS temperature program was as follows: initial temperature 50 °C, held for 2 min, then increased by 10 °C min^{-1} to 300 °C and held for 3 min. OCP standards and samples were analysed in selective ion monitoring mode (SIM) with a detector voltage of 1.5 kV and a scan range of m/z 50–500. The most abundant ion present was selected as the quantitative ion, while a further two ions were used for confirmation of individual pesticide compounds, as listed in Table 1. A clean well resolved chromatogram was obtained for spiked artificial seawater sample after extraction (Fig. 2).

3. Results and discussion

3.1. Optimization of liquid-phase microextraction

In order to optimize the liquid-phase hollow fibre extraction of OCPs from aqueous samples, analytical

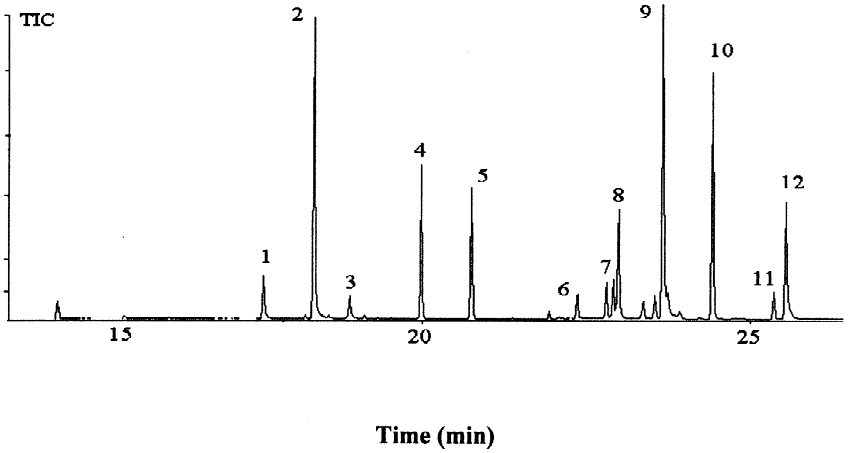

Fig. 2. Chromatogram of 12 OCPs in an OCP spiked (40 μg l^{-1}) in artificial seawater sample after LPME using hollow fibre membrane. Peaks: 1=α-BHC; 2=lindane; 3=α-BHC; 4=heptachlor; 5=aldrin; 6=dieldrin; 7=endrin; 8=endosulfan; 9=*p,p′*-DDT; 10=*p,p′*-DDD; 11=endrin aldehyde; 12=methoxychlor.

factors that potentially affect sample extraction were studied. Such factors included sample pH, salt content and stirring rate, as well as solvent type and extraction time. Sample extraction yield was determined by chromatographic peak area analysis and the analyte enrichment factor, defined as the peak ratio of analytes in solvent before and after liquid-phase microextraction. A sample (40 μg l^{-1}) of each OCP was added to 5 ml of purified water. The analytical factors were evaluated by analysis in triplicate.

The enrichment factor E_f was calculated based on the equation

$$E_f = 1/(V_o/V_a + 1/K)$$

In this equation K is the distribution coefficient, V_o is volume of organic solvent and V_a is volume of aqueous sample. K is calculated based on the two-phase equilibrium condition

$$K = C_{o\,eq}/C_{a\,eq}$$

where $C_{o\,eq}$ is the concentration of analyte in the organic phase and the $C_{a\,eq}$ is the concentration of analyte in the aqueous phase. The optimum conditions were applied to investigate the enrichment factors of analytes. Compared to LLE and SPE methods [25–27] LPME gave satisfactory sensitivity and enrichment factors of between 63 and 139 (Table 2) for OCPs. In addition, solvent consumption was reduced by up to 200 times.

3.1.1. Solvent selection

Selection of a suitable solvent is a critical parameter in LPME. The range of solvents suitable for use with hollow fibre membranes is limited as the solvent must have low solubility in water, and analytes must, of course, be soluble in it. The solvent should also have low volatility to prevent evaporation during extraction [28]. In this study five different solvents were evaluated, i.e. toluene (polarity index, 2.4), dichloromethane (3.1), *n*-hexane (0.1), isooctane (0.1) and *n*-nonane (no polarity index available) [29]. A large OCP enrichment factor may be expected if a solvent has a high partition coefficient and stability in the porous membrane. The data indicated in Fig. 3 show that among the solvents considered, toluene and *n*-nonane provide higher enrichment factor for most of the analytes. Isooctane and *n*-hexane were the least effective solvents. Dichloromethane is not suitable as it readily leaked from the porous membrane of the hollow fibre, evaporates quickly and is relatively soluble in water (~2%, v/v) resulting in loss of analyte.

3.1.2. Extraction time

The effect of extraction time on the OCP enrichment factor was evaluated from GC peak areas. Fig. 4 shows that most OCPs, i.e. α-BHC, lindane, β-BHC, heptachlor, aldrin, dieldrin, endosulfan, *p,p′*-DDD, *p,p′*-DDT, endrin aldehyde and methoxy-

Table 2
OCP linearity range, and detection limits, enrichment factor and precision level (%RSD) of LPME relative to EPA Method 508

Pesticide	Correlation coefficient	Equation	Linearity ($\mu g\ l^{-1}$)	Enrichment factor	Detection limit ($\mu g\ l^{-1}$)	EPA Method 508[a] detection limit ($\mu g\ l^{-1}$)	RSD (%)
α-BHC	0.9995	$y = 17\,591x - 83\,837$	5–100	139	0.017	0.025	13.72
Lindane	0.9991	$y = 103\,779x - 315\,230$	5–100	74	0.013	0.010	14.00
β-BHC	0.9963	$y = 3197.9x - 31\,431$	5–100	83	0.029	0.025	10.29
Heptachlor	0.9905	$y = 38\,755x - 222\,088$	5–100	113	0.030	0.010	1.90
Aldrin	0.9915	$y = 42\,758x - 233\,641$	5–100	105	0.059	0.075	2.01
Dieldrin	0.9944	$y = 10\,591x - 47\,119$	5–100	92	0.047	0.010	2.32
Endrin	0.9995	$y = 4736.6x - 12\,678$	5–100	98	0.033	0.025	1.93
Endosulfan	0.9991	$y = 6425.4x - 23\,707$	5–100	155	0.028	0.015	3.13
p,p'-DDD	0.9911	$y = 110\,363 - 440\,623$	5–100	67	0.028	0.003	2.28
p,p'-DDT	0.9958	$y = 34\,204x - 81\,004$	5–100	68	0.017	0.060	1.66
Endrin aldehyde	0.9973	$y = 15\,599x - 50\,147$	5–100	69	0.031	0.024	5.50
Methoxychlor	0.9884	$y = 34\,322x - 190\,574$	5–100	63	0.041	0.050	1.60

[a] Ref. [26].

chlor, attained equilibrium after 30 min, while endrin reached equilibrium after only 20 min (Fig. 4). On the basis of the results obtained an extraction time of 30 min was selected for real seawater analysis.

3.1.3. Effect of sample pH on OCP extraction

The effect of pH on OCP extraction efficiency was evaluated. A reduction in sample pH is known to improve extraction efficiency of polar compounds such as phenols [30]. The effect of sample pH in the range of 2–13 on OCP extraction was measured by adding 6 *M* HCl and 10% (w/v) NaOH to the samples. Extraction efficiency of most OCPs was not affected over the pH range studied, with the exception of aldrin, dieldrin, endrin, p,p'-DDD, p,p'-DDT and methoxychlor which had a higher extraction efficiency at a lower pH. The other OCPs (α-BHC, β-BHC, lindane, heptachlor, endrin aldehyde) had a reduced extraction efficiency at more alkaline pH range (data not shown). These compounds are known to decompose at an alkaline pH

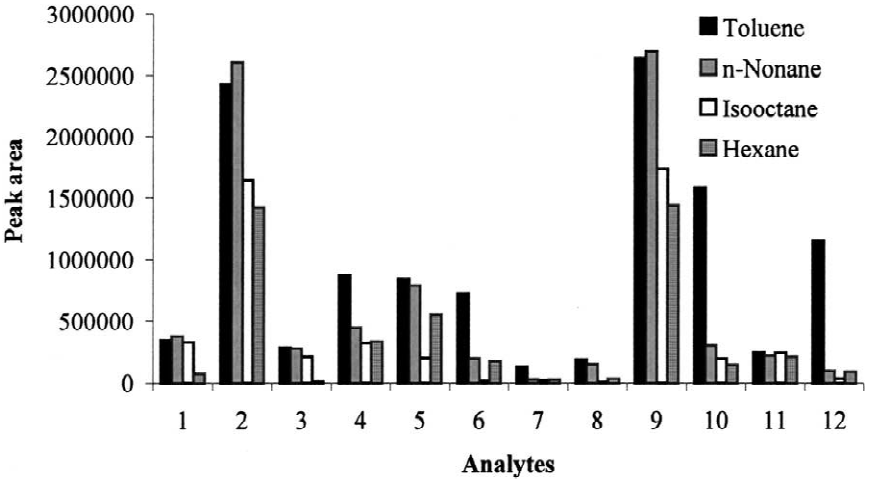

Fig. 3. OCP extraction efficiency from spiked (40 $\mu g\ l^{-1}$) artificial seawater using different organic solvents ($n = 3$). Peak identification as in Fig. 2.

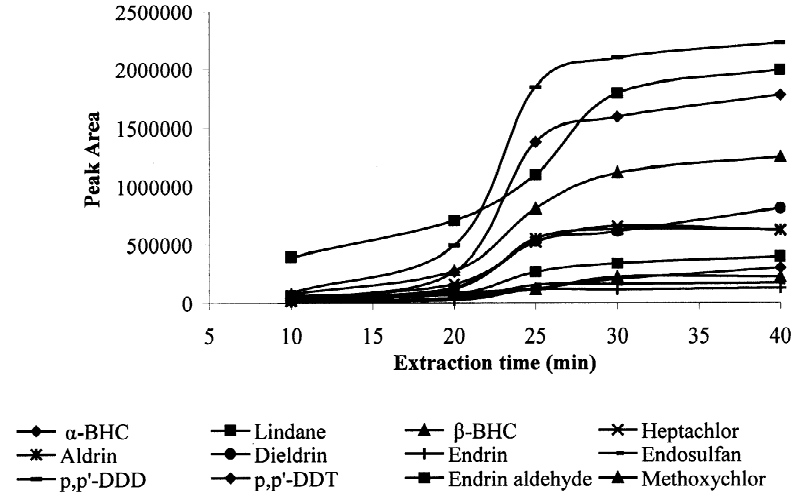

Fig. 4. Equilibration profile of OCPs during LPME with hollow fibre membrane extraction.

[31], which may account for the result obtained. On the basis of these results, a pH of 2 was used for real seawater analysis.

3.1.4. Sample salt concentration

The addition of salt improves the extraction recovery of OCPs in many conventional extraction techniques, and sodium chloride (NaCl) is commonly added to analytical samples [31]. In this study, the effect of adding salt was tested. There was no significant increase in extraction efficiency (Fig. 5) at higher (10% NaCl to 33% (i.e. saturated NaCl) salt concentrations. Thus, real seawater (3% salt) was used directly without further salt addition.

3.1.5. Sample agitation rate

The effect of sample agitation was evaluated using a stirring speed of between 100 and 1200 rpm.

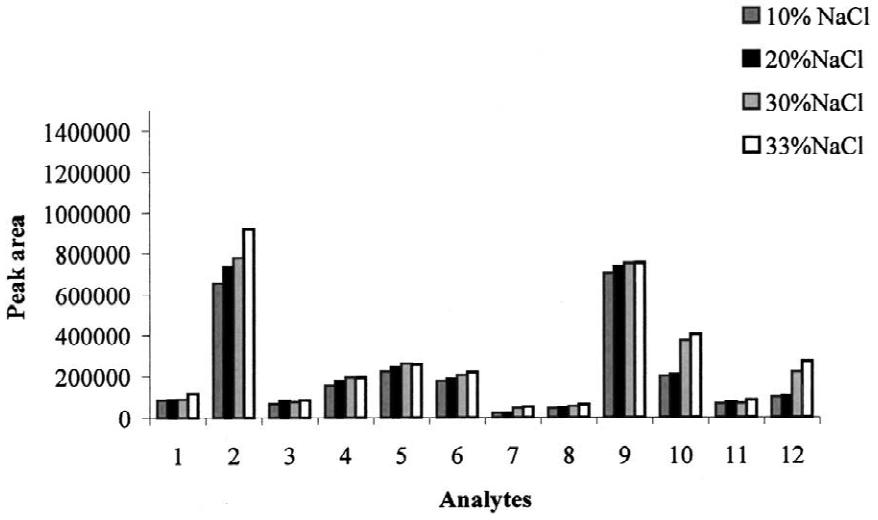

Fig. 5. Effect of artificial seawater concentration (10% NaCl to saturated NaCl) on OCP extraction efficiency. Peak identification as in Fig. 2.

Sample agitation improved OCP extraction efficiency, where relative chromatographic peak areas increased with stirring rate. However, above 900 rpm, although extraction efficiency was better for some analytes, air bubble formation frequently occurred, leading to quantitation problems. Therefore an optimum stirring speed of 900 rpm was selected for real seawater analysis.

3.1.6. Sample temperature

The effect of sample temperature on extraction efficiency was investigated between 25 and 60 °C. An increase in extraction temperature can be expected to increase the enrichment factor due to an increase in the OCP diffusion coefficient across the hollow fibre membrane. The equilibrium of OCP concentration was achieved faster at a higher extraction temperature, but a sample temperature above 25 °C resulted in the formation of air bubbles in the solvent in the hollow fiber. On the basis of the results obtained, an extraction temperature of 25 °C was used for seawater analysis.

3.2. Linearity, precision, and sensitivity

To evaluate the linearity of the method, artificial seawater samples were spiked with the 12 OCPs to give final sample concentrations of 5, 10, 20, 50 and 100 μg l^{-1}, and then extracted. The GC peak area counts were plotted against the respective OCP concentrations to generate calibration curves. The calibration gave a high level of linearity with a correlation coefficient of between 0.9884 and 0.9995 (Table 2). Limits of detection (LODs), defined as the lowest concentrations of the analytes that produce chromatographic peaks at $S/N=3$, were evaluated under MS-SIM conditions and found to be in the range of 0.013–0.059 μg l^{-1}, generally comparable to those of US Environmental Protection Agency (EPA) Method 508. The precision of the experimental procedure was evaluated using artificial seawater spiked with 40 μg l^{-1} of each OCP under the optimum extraction conditions. This yielded a standard deviation (RSD) of between 1.6 and 14% for a total of four replicates.

3.3. Water sample analysis

All 12 OCPs were spiked to tap and unprocessed reservoir water, as well as artificial seawater and ultrapure water samples at 40 μg l^{-1} per pesticide to assess sample matrix effects. OCP recovery was calculated from the relative peak area ratio of each type of water sample relative to the OCP-spiked ultrapure water sample. Table 3 lists the relative OCP recoveries for the respective water samples. The data show that relative recoveries for all OCPs

Table 3
OCP recoveries in spiked (40 μg l^{-1}) tap water, reservoir water and artificial seawater samples (relative to OCP-spiked ultrapure water)

Pesticide	Tap water		Reservoir water		Seawater[a]	
	Relative recovery (%)	RSD (%)	Relative recovery (%)	RSD (%)	Relative recovery (%)	RSD (%)
α-BHC	93.64	±1.11	91.67	±6.89	90.82	±4.28
Lindane	86.52	±1.10	84.13	±5.83	83.90	±9.86
β-BHC	85.35	±0.84	91.27	±6.02	90.61	±11.93
Heptachlor	97.36	±0.93	93.15	±4.51	94.70	±9.39
Aldrin	89.45	±1.08	83.65	±3.42	80.90	±4.24
Dieldrin	91.44	±1.20	97.14	±3.59	88.60	±8.75
Endrin	93.68	±1.14	77.33	±10.87	82.50	±2.63
Endosulfan	92.02	±1.14	93.33	±13.36	93.33	±11.92
p,p′-DDD	95.24	±1.07	92.13	±3.47	87.91	±8.43
p,p′-DDT	94.73	±0.99	81.67	±2.79	83.53	±11.38
Endrin aldehyde	90.00	±1.04	89.33	±10.08	91.76	±13.00
Methoxychlor	97.04	±1.09	99.90	±6.73	92.59	±8.14

For each OCP, 40 μg l^{-1} were spiked ($n=3$).
[a] Artificial seawater.

Table 4
OCP concentrations (μg l^{-1}) in seawater samples collected from the Straits of Johore: Kranji (J05), Lim Chu Kang (J01), Pulau Ubin (J09), and Pulau Tekong (H01)

Pesticide	Sampling location (concentration μg l^{-1})			
	J05	J01	J09	H01
α-BHC	0.043	0.180	ND	0.075
Lindane	0.057	0.228	ND	0.107
β-BHC	1.094	0.585	ND	0.098
Heptachlor	0.233	0.394	ND	0.205
Aldrin	0.251	0.333	0.446	0.049
Dieldrin	0.255	0.315	0.333	0.977
Endrin	0.624	0.044	0.041	1.270
Endosulfan	0.899	0.077	0.312	0.068
p,p′-DDD	0.564	0.550	0.563	0.132
p,p′-DDT	0.608	0.808	0.744	0.038
Endrin aldehyde	0.241	0.010	0.147	0.486
Methoxychlor	0.053	0.108	0.098	0.616

ND, not detected.

were between 80 and 99% with an RSD of less than 14%.

Coastal seawater samples collected from the sea surface in the Straits of Johor, located between Singapore and the Malaysian peninsula, were also analysed using the optimised LPME technique, and the results are shown in Table 4. In general, OCP concentrations in seawater were found to be much lower than reported elsewhere, for example, in Australian marine waters [32]. This is not unexpected, as extensive agricultural activities in Singapore have been phased out for more than two decades. Although some minimal agricultural activities remain, they generally do not involve extensive use of the types of pesticides discussed in the present work. Fig. 6 shows a typical chromatogram generated from real seawater sample.

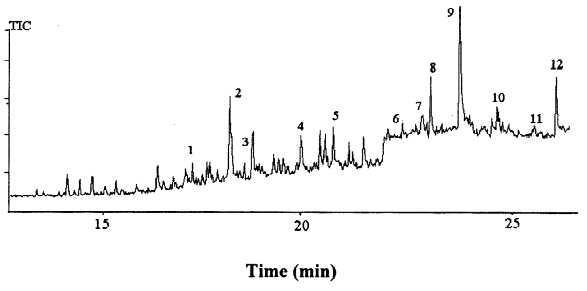

Fig. 6. Chromatogram of OCPs extracted from real seawater collected from the Straits of Johore. Peak identification as in Fig. 2.

4. Conclusion

The optimised LPME technique using hollow fibre membrane in conjunction with GC–MS is a simple, solvent minimising and cost effective procedure for analysis of OCPs in seawater. The method is precise, reproducible and has a high level of linearity over a wide range of analyte concentrations. Optimised extraction procedures enabled the quantification of OCPs at analyte concentrations in the sub-parts per billion range, comparable to EPA Method 508. Sample clean-up was highly effective, with no interfering peaks from matrix compounds. The method has a proven viability for quantitative analysis of OCPs in real seawater samples.

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